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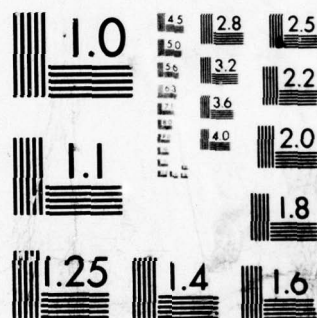
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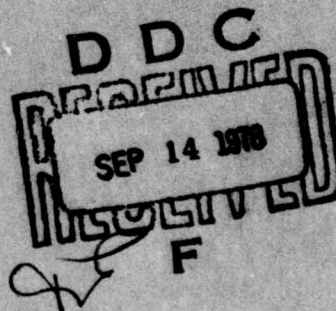
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Effect of Vibrational Excitation in Reactions of OH with H₂

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El Segundo, Calif. 90245

15 August 1978

Interim Report



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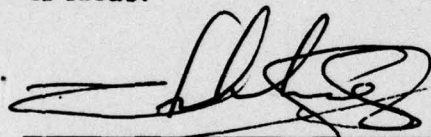
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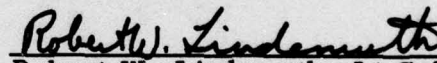
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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


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PREFACE

The authors are glad to acknowledge stimulating discussions with Dr. R. R. Herm and Dr. R. J. McNeal during the analysis of the results.

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FIGURE

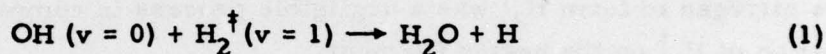
1. Dependence of Relative Hydroxyl Density $\text{OH}(v = 0)$ and $\text{OH}^\dagger(v = 1)$ on Absolute Density of Vibrationally Excited Hydrogen $\text{H}_2^\dagger(v = 1)$	9
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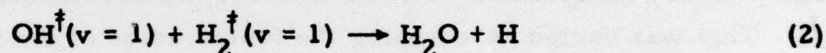
I. Introduction

Recently, a measurement of the rate of the reaction between $O(^3P)$ and $H_2^{\dagger}(v = 1)$ has appeared in the literature,¹ and an upper limit to the rate of $OH^{\dagger}(v = 1) + H_2(v = 0)$ has been given.²

These reports are beginning to characterize the effects of vibrational energy in the diatomic molecules of the H_2/O_2 system. This work extends this beginning by reporting upper limits to the reaction rates for two reactions:

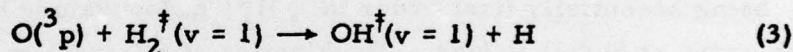


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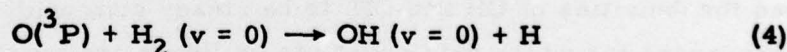


II. Experiment

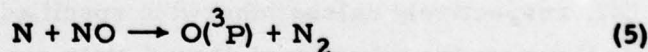
The experimental apparatus has been fully described elsewhere.^{1,3} Briefly, the measurements were obtained in a laboratory flow tube apparatus at a total pressure of 3 Torr consisting of equal parts N_2 and H_2 at a temperature of 298 K. Vibrationally excited hydroxyl was produced entirely by reaction (3)



Vibrational ground state hydroxyl was produced predominantly by physical quenching of $OH^{\dagger}(v = 1)$. At lower concentrations of $H_2^{\dagger}(v = 1)$ there were minor contributions from reaction (4),



Atomic oxygen was produced by reaction (5), for which the N atoms were provided by a microwave discharge in N_2



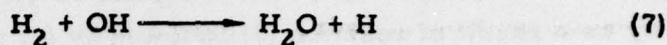
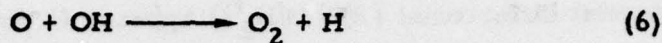
The flow rate of nitric oxide was adjusted so that operation at the visible titration end point was achieved. Vibrationally excited hydrogen* was generated by the flow of hydrogen over a heated tungsten filament. The density of H_2^\dagger was determined from spectral absorption measurements in the Lyman band system of hydrogen. Hydroxyl densities were deduced from laser induced fluorescence (LIF) in the ($A^2\Sigma \rightarrow X^2\Pi$) system of OH. Measurements were conducted under conditions where energy transfer^{1,3} from active nitrogen to form H_2^\dagger was a negligible process in comparison with the formation of H_2^\dagger on the heated filament.

The primary independent variable in these measurements was the density of H_2^\dagger . This was varied by changing the temperature of the tungsten heating element.

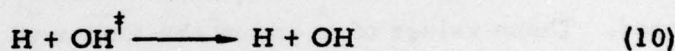
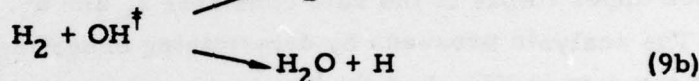
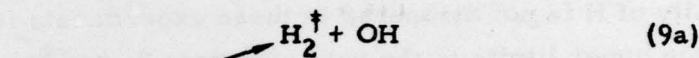
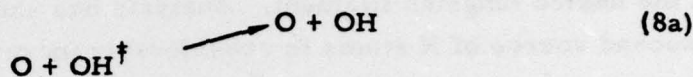
III. Results and Analysis

Fig. 1 shows data for the dependence of OH and OH^\dagger densities on $[H_2^\dagger]$. It is seen that the density of OH is first order in $[H_2^\dagger]$ at the larger values of $[H_2^\dagger]$ but tends toward zeroth order as $[H_2^\dagger]$ decreases. The OH at low values of $[H_2^\dagger]$ comes from reaction (4). The density of OH^\dagger behaves oppositely, being essentially first order in $[H_2^\dagger]$ at low values but tending toward zeroth order at higher values. The kinetics of this system have been modelled using a computer code to integrate the rate equations. Individual vibrational levels of OH^\dagger ($v \leq 3$) and H_2^\dagger were treated as separate entities with generation and removal processes individually specified. Analysis of the computer results showed the densities of OH and OH^\dagger to be steady state with the most important loss processes for which rate constants or limits are available as follows; for OH:

* Hereinafter, the symbols $H_2^\dagger(v=1)$ and $OH^\dagger(v=1)$ will be simplified to H_2^\dagger and OH^\dagger , respectively unless otherwise specified. The symbols H_2 and OH shall denote the vibrational ground state species only.



and for OH^\ddagger :



In addition, of course, it is necessary to consider the possibility that the reactions of interest, i.e., (1) and (2), contribute significantly. The important generation processes for OH were all found to be physical deactivation of OH^\ddagger . These are (8a), (9a), and (10). For OH^\ddagger , the important source terms are reactions (3) and (-9a).

Using the reaction scheme outlined one can form the steady state expressions for the densities of OH and OH^\ddagger . Taking logarithms and differentiating with respect to $[\text{H}_2^\ddagger]$, expressions (a) and (b) for the slopes of plots of $\log [\text{OH}(v)]$ versus $\log [\text{H}_2^\ddagger]$ are derived.

$$\frac{d(\log[\text{OH}^\ddagger])}{d(\log[\text{H}_2^\ddagger])} \equiv m^\ddagger = 1 - \left(\frac{k_2 + k_{10} \left(\partial[\text{H}]/\partial[\text{H}_2^\ddagger] \right)}{k_8[\text{O}]/[\text{H}_2^\ddagger] + k_9[\text{H}_2]/[\text{H}_2^\ddagger] + k_{10}[\text{H}]/[\text{H}_2^\ddagger] + k_2} \right) \quad (a)$$

$$\frac{d(\log[\text{OH}])}{d(\log[\text{H}_2^\ddagger])} \equiv m = m^\ddagger +$$

$$\left(\frac{k_{10} \partial[\text{H}]/\partial[\text{H}_2^\ddagger]}{k_{8a}[\text{O}]/[\text{H}_2^\ddagger] + k_{10}[\text{H}]/[\text{H}_2^\ddagger] + k_{9a}[\text{H}_2]/[\text{H}_2^\ddagger]} \right) - \left(\frac{k_1}{k_1 + k_7[\text{H}_2]/[\text{H}_2^\ddagger] + k_6[\text{O}]/[\text{H}_2^\ddagger]} \right) \quad (b)$$

The partial differential ($\partial[H]/\partial[H_2^\ddagger]$) appears in both expressions and requires some explanation. $[H]$ will depend on $[H_2^\ddagger]$ in two ways; first, directly as a result of reaction (3) followed by (6) through (10), and secondly, in an indirect way, since H_2 is thermally partially dissociated in contact with the heated tungsten filament. Analysis has shown that for large $[H_2^\ddagger]$ the second source of H atoms is considerably more important than the first if one assumes that both H and H_2^\ddagger are present in amounts determined by equilibrium at the filament temperatures. Because of this and because the density of H is not measured in these experiments it is only possible to deduce upper limits to the rate constants k_1 and k_2 .

The analysis proceeds by determining experimental values of m and m^\ddagger from the data in Fig. 1 at the maximum value of $[H_2^\ddagger]$ where data were obtained. These values of m and m^\ddagger are then used in expressions (a) and (b) to find mutually consistent sets of values for $[H]$, $\partial[H]/\partial[H_2^\ddagger]$, and the unknown rate constants k_1 , k_2 , k_{9a} and k_{9b} . These unknown values were allowed to vary throughout their respective ranges of uncertainty. It was found that there were certain values of k_1 and k_2 which could never be exceeded irrespective of the values assigned to the other uncertain quantities in expressions (a) and (b). These values of k_1 and k_2 are necessarily upper limits and are the values reported herein.

In this analysis values for $[H]$ and $\partial[H]/\partial[H_2^\ddagger]$ were allowed to vary from zero upwards to the values dictated by thermal equilibrium at the filament temperature. However, the ratio of the terms was constrained by expression (c), which is a consequence only of the assumption of thermochemical equilibrium irrespective of temperature.

$$\partial[H]/\partial[H_2^\ddagger] = \frac{(\Delta H^\circ)_r}{2G_0(1)} \left(\frac{[H]}{[H_2^\ddagger]} \right) \quad (c)$$

where $(\Delta H^\circ)_r$ is the heat of reaction for dissociation of H_2 and $G_0(1)$ is the energy of the first vibrational state of H_2 above that of the ground state.

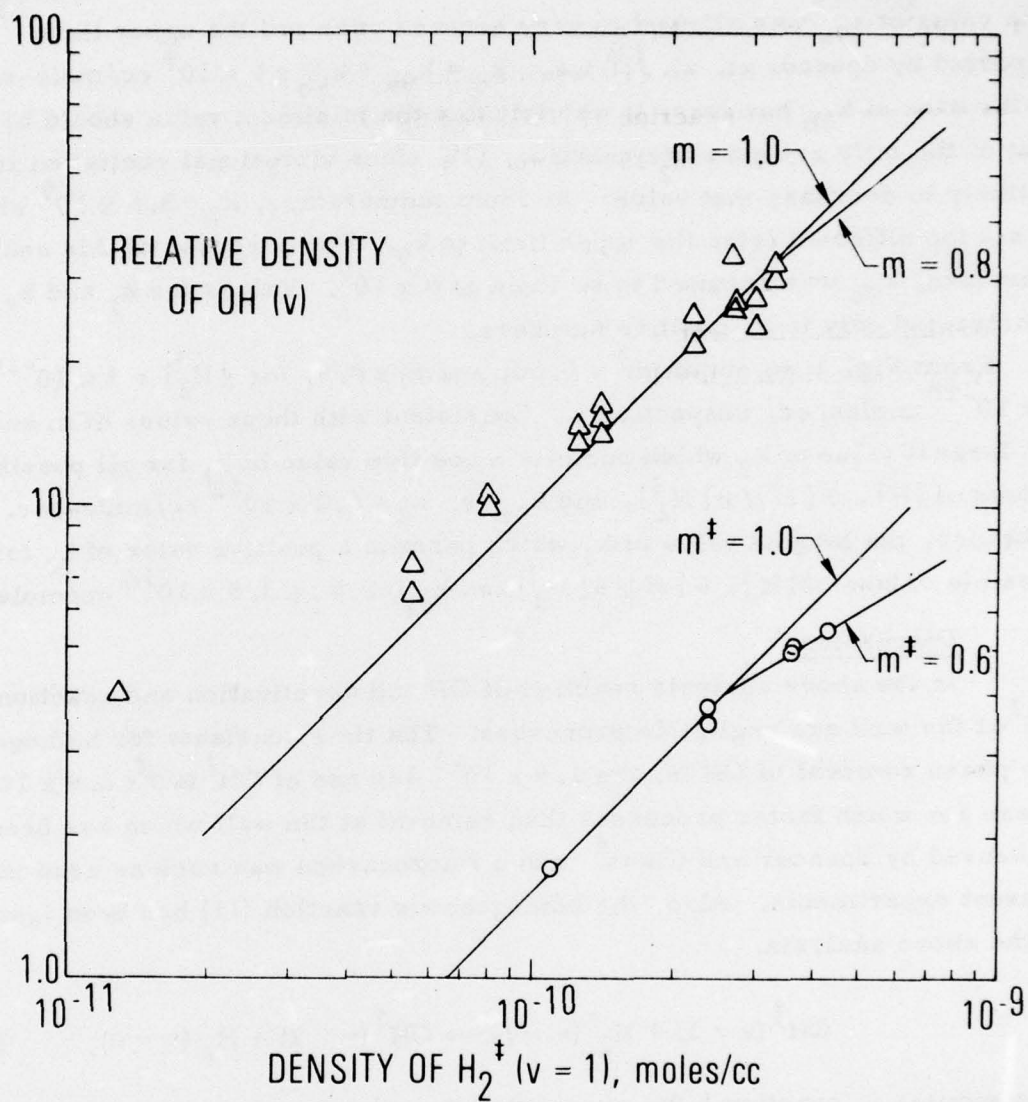


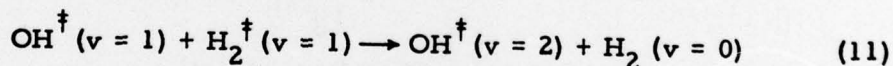
Fig. 1. Dependence of Relative Hydroxyl Density $OH(v = 0)$ and $OH^\dagger(v = 1)$ on Absolute Density of Vibrationally Excited Hydrogen $H_2^\dagger(v = 1)$. (Δ) $OH(v = 0)$; (\odot) $OH^\dagger(v = 1)$.

The value of k_{9a} was allowed to vary between zero and the upper limit reported by Spencer et. al.,⁽²⁾ i.e., $k_9 = k_{9a} + k_{9b} \leq 6 \times 10^9$ cc/mole-sec. In the case of k_{9b} however, it was felt that the minimum value should be that of the fully ground state reaction, (7), since vibrational excitation is unlikely to decrease that value. At room temperature, $k_7 = 3.6 \times 10^9$ which is not too different from the upper limit to k_9 . For purposes of this analysis therefore, k_{9b} was assumed to be fixed at 6×10^9 . Values for k_1 and k_2 were constrained only to be positive numbers.

From Fig. 1 we obtain $m^\ddagger = 0.60$, and $m \geq 0.8$, for $[H_2^\ddagger] = 4 \times 10^{-10}$ and 3×10^{-10} moles/cc, respectively. Consistent with these values of m and m^\ddagger the largest value of k_2 which permits a positive value of k_1 for all possible values of $[H]$, $\partial [H]/\partial [H_2^\ddagger]$, and k_{9a} is: $k_2 \leq 6.2 \times 10^{12}$ cc/mole-sec. Likewise, the largest value of k_1 which permits a positive value of k_2 for all possible values of $[H]$, $\partial [H]/\partial [H_2^\ddagger]$ and k_{9a} is: $k_1 \leq 3.5 \times 10^{12}$ cc/mole-sec.

IV. Discussion

In the above analysis reaction of OH and deactivation and reaction of OH^\ddagger at the wall are negligible processes. The time constants for homogeneous gas phase removal of OH is, $\tau \leq 1.6 \times 10^{-3}$ sec and of OH^\ddagger is $\tau^\ddagger \leq 2.4 \times 10^{-4}$ sec. These are much faster processes than removal at the wall which has been measured by Spencer and Glass⁴ with a fluorocarbon wax such as used in the present experiments. Also, the homogeneous reaction (11) has been ignored in the above analysis.



It is similar to reaction (-9a) except that the vibrational energy exchange is further from resonance for (11) than it is for (-9a). Using the upper limit² for k_{9a} and the principle of microscopic reversibility it is necessary that

$$k_{(-9a)} \leq 10^{11} \text{ cc/mole-sec.}$$

It is not likely that reaction (11) would be greatly faster than this and so it is reasonable to ignore it in the above analysis.

The effect of vibrational excitation in OH on the reaction with H_2 was found by Spencer et. al.² to be minor, such that $(k_{9a} + k_{9b})/k_7 < 1.7$. We have not been able to measure or find lower limits for the effect of vibrational excitation in H_2 on this reaction. It seems likely that this reaction proceeds by breaking of the H_2 bond rather than of the OH bond since the latter course requires the insertion of O between H atoms in order to form water. If this is true one would expect that vibrational energy in hydrogen would be much more effective in promoting the reaction than would vibrational energy in OH. The results reported here and by Spencer et. al. are at least consistent with this view.

Our results indicate that $k_1/k_7 \leq 1000$ and that $k_2/k_7 \leq 1800$ at $T = 298$ K. Thus, there is room still for appreciable acceleration of the reaction by one quantum of vibrational energy in H_2 or by one quantum in both OH and H_2 . Zellner⁵ has determined a preliminary result of $k_1 \approx (3.6 \pm 1.8) \times 10^{11}$ cc/mole-sec, corresponding to an increase of roughly a factor of 100 over the ground state reaction. This result is consistent with our upper limits and with the view sketched above.

From the upper limits for k_1 and k_2 reported here and from the upper limit for k_{9b} it is clear that one quantum of vibrational energy in either OH or in H_2 or in both simultaneously is not as effective in promoting the reaction as is the same specific energy equipartitioned between all modes of both reactants.

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2. J. E. Spencer, H. Endo, G. P. Glass, Proc. 16th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 15 - 20 August, (1976).
3. G. C. Light, Proc. 17th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa. 21 - 25 August, (1978), to be published.
4. J. E. Spencer, G. P. Glass, Chem. Phys. 15, 35 (1976).
5. R. Zellner, private communication.

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